

TITLE OF THE INVENTION

PORPHYRIN ARRAY EXHIBITING LARGE TWO PHOTON ABSORPTION
PROPERTY AND INCLUDING, AS STRUCTURAL UNIT,
BIS(IMIDAZOLYLPORPHYRIN METAL COMPLEX) LINKED WITH
5 ACETYLENIC BOND AND THE DERIVATIVE THEREOF, AND METHOD
OF PRODUCING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the
benefit of priority from the prior Japanese Patent
10 Application No. 2002-335246, filed November 19, 2002,
the entire contents of which are incorporated herein by
reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

15 The present invention relates to porphyrin metal
complexes which can serve as two-photon absorption
materials, and derivatives thereof. More specifically,
the present invention relates to porphyrin arrays which
exhibit large two-photon absorption, and having, as a
20 structural unit, bis(imidazolyldiporphyrin metal complex)
linked with an acetylic bond, and derivatives thereof.
The present invention also relates to porphyrin arrays
having, as a structural unit, the
bis(imidazolyldiporphyrin metal complex) that is further
25 fixed with covalent bonds.

2. Description of the Related Art

It is expected that a two-photon absorption

material will be applied to various applications such as three-dimensional optical memory, photodynamic therapy, optical limiting materials, and a two-photon microscopy. Among these applications, three-
5 dimensional optical memory which enables ultrafast reading and writing with a very high density, and photodynamic therapy in which only cancer cells are selectively attacked by laser for medical treatment, are particularly important in view of a great
10 contribution to the society.

In designing an organic compound exhibiting a relatively large two-photon absorption cross section, it is presumably very important that π -electron conjugated system is expanded thereby the overlap of
15 the orbitals is increased, and polarization of the molecule is enhanced by appropriately combining an electron donor and an electron acceptor. As porphyrin is a ring-shaped tetra pyrrole in which four pyrrole nucleuses are cross-linked by four methine groups, and
20 has a large conjugated system including 18 π -electrons, porphyrin is one of the promising candidates of the two-photon absorption materials.

The phenomenon of two-photon absorption itself has been known for years, but advanced research on two-
25 photon absorption has finally begun since Jean-Luc Brédas et al. revealed the relationship between the molecular structure and the mechanism of two-photon

absorption in 1998 (Science, 281, 1653 (1998)).

However, there are few reports on the two-photon absorption of porphyrin. Quite recently, Anderson reported that a one-dimensional linear porphyrin

5 polymer, in which porphyrins are linked with butadiyne bonds, exhibits a relatively large two-photon absorption cross section (J. Am. Chem. Soc., 124, 9712 (2002)). However, the length of the polymer cannot be adjusted, because covalent bonds are used for the

10 linkages in the porphyrin polymer. Further, as introduction of hetero metals thereto and introduction of electron donors/electron acceptors to the terminal groups thereof is difficult, the two-photon absorption property of the porphyrin polymer cannot be further

15 improved. Yet further, in Anderson's case, the two-photon absorption property is measured on the time scale of picoseconds, and the analysis of two-photon absorption in the order of femtoseconds, which

essentially requires for an ultra fast recording, has not been carried out. As long as covalent bonds are used for the linkage of porphyrins, introduction of electron donors or electron acceptors, which enables large two-photon absorption, to a one-dimensional

20 linear porphyrin array, was difficult. Therefore, in

25 the conventional method of preparing porphyrin arrays, there is no prospect of achieving large two-photon absorption.

BRIEF SUMMARY OF THE INVENTION

One object of the present invention is to provide a material exhibiting large two-photon absorption, capable of simply controlling the molecular length by utilizing a coordinate bond-based self-organization reaction, which was impossible by using a covalent bond, and capable of attaching electron acceptor molecules or electron donor molecules at terminals of the molecule.

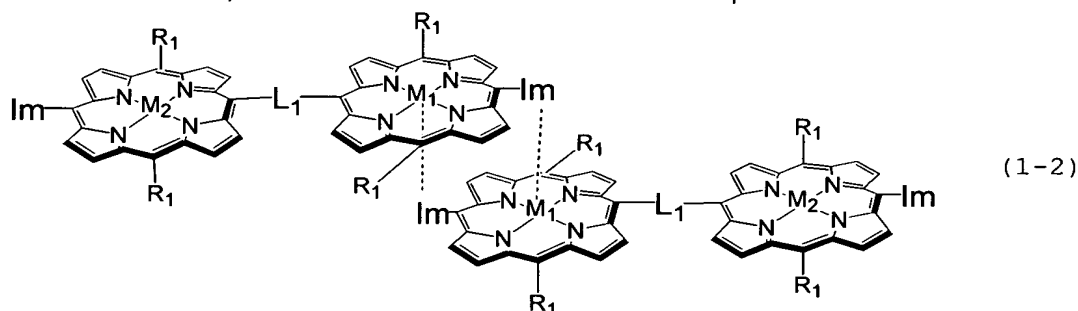
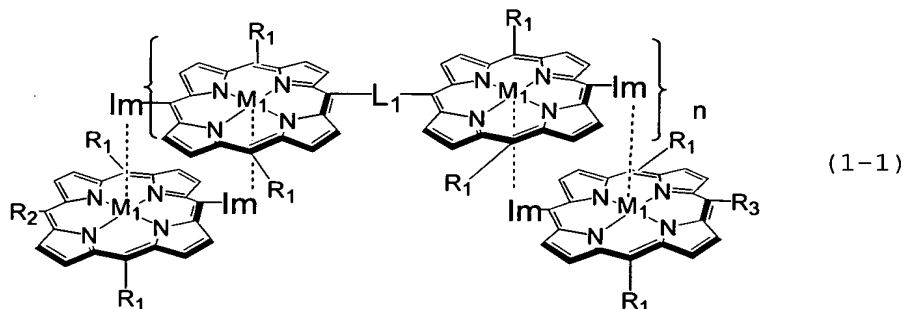
In order to achieve the objects described above, the inventors of the present invention at first linked two imidazolyl porphyrins, i.e., two porphyrins to each of which an imidazolyl group is attached, with an acetylenic bond, thereby to prepare a bis-acetylen-type dimer. Then, the inventors prepared mono-metalated complex of the bis-acetylen-type dimer, i.e., one of which is a metal complex, as a donor, and the other of which is a free base porphyrin, as an acceptor. Above mentioned two mono-metalated complexes gave a dimer formed by coordinate bonds. Prior to the discovery on which the present invention is based, the inventors had discovered the followings. That is, by coordinating a metal atom of one imidazolylporphyrin metal complex with a nitrogen atom of an imidazolyl group of another imidazolylporphyrin metal complex, a coordinated imidazolylporphyrins was prepared. Then, effecting meso-type crosslinking between two coordinated imidazolylporphyrin dimers, a meso-type poly(porphyrin)

in which imidazolylporphyrin dimers were linked by coordinate bonds was prepared. It was found that the coordinate bonds of the thus prepared meso-type poly(porphyrin) can be formed and cut off by adding and removing methanol or pyridine thereto and therefrom, respectively. In order to evaluate the effect of expanding the conjugated system by the bis-acetylenic bond on the two-photon absorption property, the inventors compared an self-assembly formed with two mono-metalated-bis-acetylen-type dimeric porphyrins having free base porphyrins serving as electron acceptors at terminals thereof with another self-assembly formed with two mono-metalated-meso-type dimeric porphyrins. It was revealed that the self-assembly constituted of two mono-metalated-bis-acetylen-type dimers, whose conjugation system had been expanded, exhibited approximately 20 times larger two-photon absorption than the self-assembly constituted of a mono-metalated-meso-type porphyrin dimers, whose conjugation system had not been expanded. The present invention has been completed on the basis of the aforementioned discoveries.

The present invention provides: a porphyrin array exhibiting a large two-photon absorption property and being linked with an acetylenic bond represented by the following formula (1-1) or (1-2); and a method of producing the porphyrin array set forth below.

(1) A porphyrin array exhibiting a large two-photon absorption property, and being linked with an acetylenic bond(s), represented by formula (1-1) or (1-2):

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In the formulas (1-1) and (1-2),

R_1 represents a substituted or unsubstituted alkyl group or substituted or unsubstituted aryl group;

15

M_1 represents a metal ion capable of serving as a core metal of the porphyrin ring and forming a coordinate bond with the imidazolyl group represented by Im; M_2 represents either two protons or a metal ion incapable of forming a coordinate bond with the imidazolyl group represented by Im;

20

R_2 and R_3 may be the same or different, and each independently represent a group selected from the group

consisting of (a) to (f):

(a) a porphyrin residue without a core metal or porphyrin complex residue having a core metal represented by M_1 or M_2 , (b) a cyclic diimide residue, (c) a dialkylviologen residue, (d) a benzoquinone residue, (e) an N-methylpyrrolidine-fullerene derivative residue and (f) a ferrocene residue;

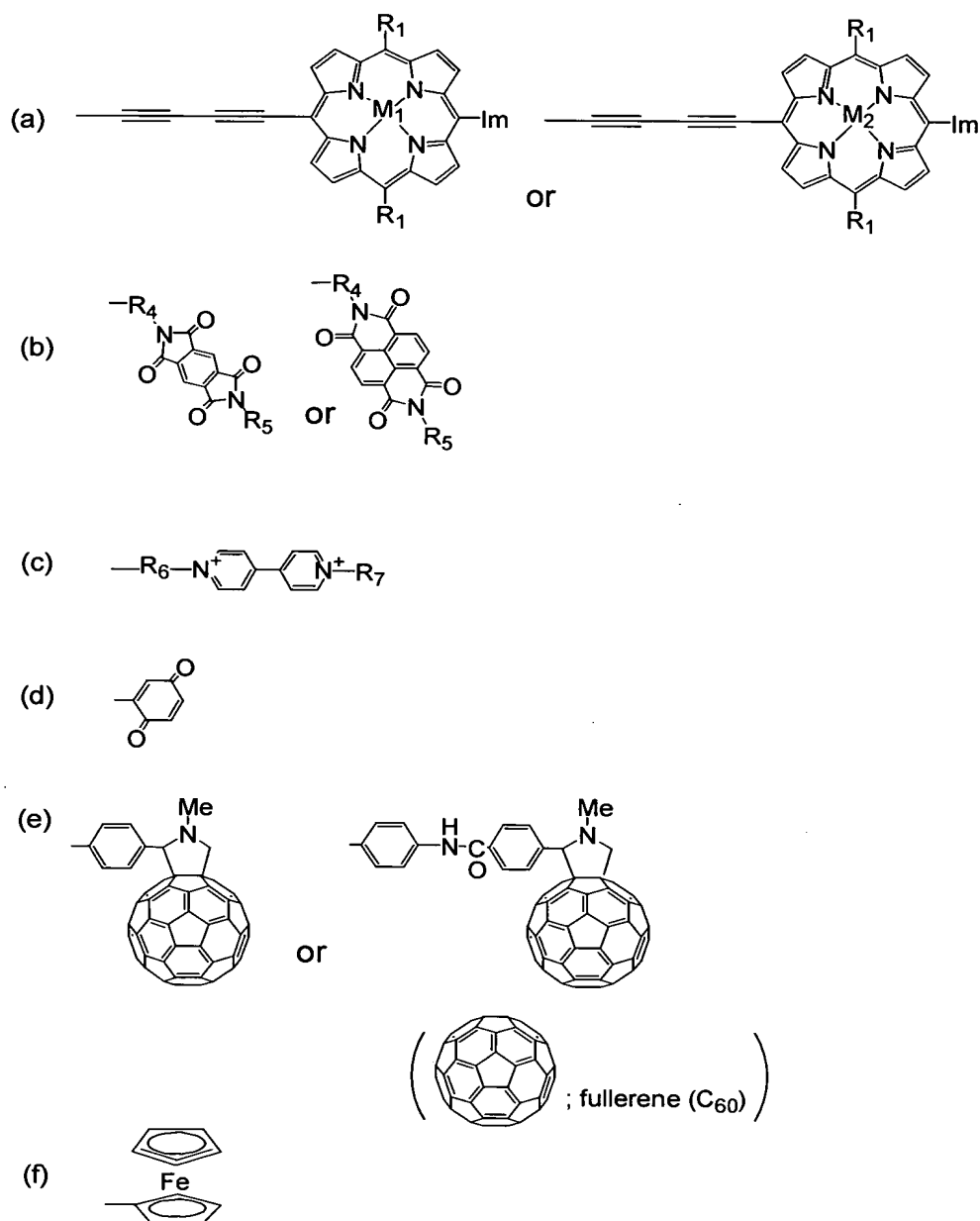
Im is an imidazolyl group represented by Im_1 or Im_2 :



(wherein R_8 represents a methyl group or hydrogen atom); L_1 represents a linking group represented by $(-C\equiv C-)_m$ (wherein m represents an integer of 1 to 3); and

n represents an integer of 1 or more.

(2) The porphyrin array described in the aforementioned (1), wherein the residues (a), (b), (c), (d), (e) and (f) are represented by:



wherein R_1 , M_1 , M_2 and Im have the same meaning as defined in the aforementioned (1), R_4 and R_6 each independently represent an alkylene group or arylene group, and R_5 and R_7 each independently represent an alkyl group, alkoxyalkyl group, alkoxycarbonyl group or aryl group.

(3) The porphyrin array described in the

aforementioned (1) or (2), wherein, M_1 is an ion of metal selected from the group consisting of zinc, iron, cobalt, ruthenium and gallium.

5 (4) The porphyrin array described in any one of the aforementioned (1) to (3), wherein the substituted alkyl group represented by R_1 is selected from the group consisting of an alkoxy carbonyl alkyl group, alkoxy alkyl group, alkenoxy alkyl group and an alkenoxy carbonyl alkyl group, and the substituted aryl
10 group represented by R_1 is selected from the group consisting of an alkyl aryl group, alkoxy aryl group, alkoxy carbonyl aryl group, alkenoxy aryl group and alkenoxy carbonyl aryl group.

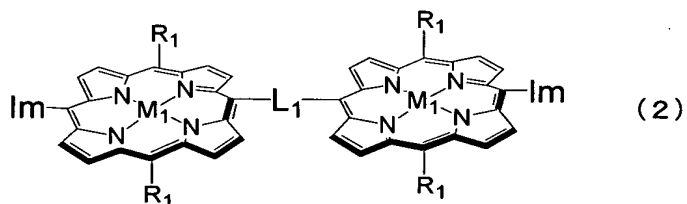
15 (5) The porphyrin array described in any one of the aforementioned (1) to (4), wherein the number of carbon atoms of the substituted or unsubstituted alkyl group represented by R_1 is 1 to 24, and the number of carbon atoms of the substituted or unsubstituted aryl group represented by R_1 is 6 to 24.

20 (6) The porphyrin array described in any one of the aforementioned (1) to (5), wherein the number of carbon atoms of the alkyl group or the alkylene group represented by R_4 to R_7 is 1 to 20, the number of carbon atoms of the alkoxy alkyl group or the
25 alkoxy carbonyl group represented by R_5 and R_7 is 2 to 21, and the number of carbon atoms of the aryl group or the arylene group represented by R_4 to R_7 is 6 to 20.

The present invention also provides a method of preparing the porphyrin array as follows:

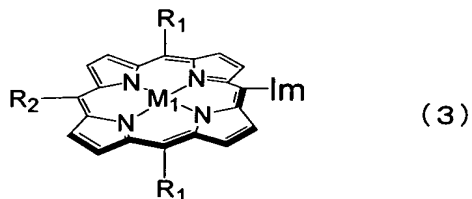
(7) A method of preparing the porphyrin array represented by the formula (1-1) or (1-2) described in (1) mentioned above, comprising:

reacting, in the presence of a polar solvent, an imidazolylporphyrin metal complex represented by the following formula (2),



wherein R_1 , M_1 , L_1 and Im have the same meaning as defined in (1) mentioned above

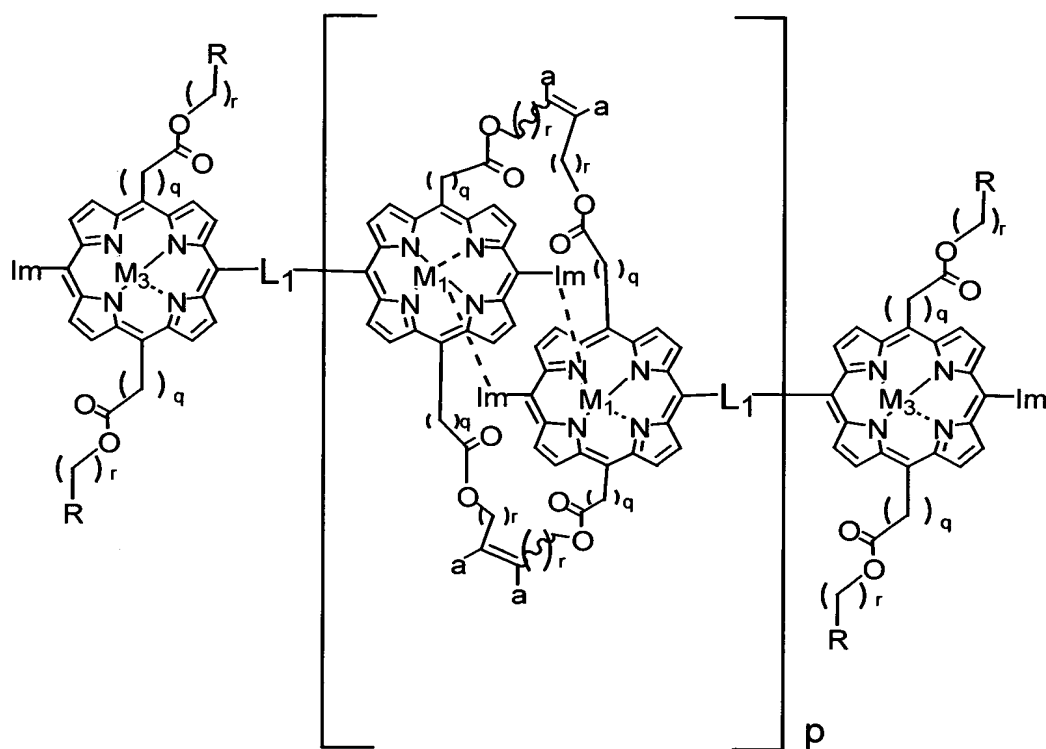
with an imidazolylporphyrin metal complex represented by the following formula (3),



wherein R_1 , R_2 , M_1 and Im have the same meaning as defined in the aforementioned (1).

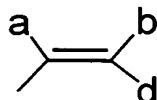
The present invention also provides a porphyrin array being linked with an acetylenic bond(s) and also being fixed with a covalent bond(s) as follows:

(8) A porphyrin array exhibiting a large two-photon absorption property, and being fixed with a covalent bond(s), represented by formula (4):



(4)

wherein R represents an alkyl group or a group as shown below:



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(wherein a, b and c independently represent H, an alkyl group or aryl group); M_1 , L_1 and Im have the same meaning as defined in (1) mentioned above; M_3 represents either two protons or a metal ion selected from the group consisting of those represented by M_1 and M_2 ; p represents an integer of 1 or more; q represents an integer of 0 to 6; and r represents an integer of 0 to 4.

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Additional objects and advantages of the invention will be set forth in the description which follows, and

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in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is two-photon absorption spectra of a porphyrin array 10 of the present invention and a reference array 12.

FIG. 2 is gel filtration column chromatogram of the polymer B-7.

FIG. 3 is MALDI-TOF mass spectrometry of the polymer B-7.

FIG. 4 is ultraviolet and visible region absorption spectrum of polymer B-7 (in chloroform).

FIG. 5 is a view of ultraviolet and visible range absorption spectrum of polymer B-7 (in pyridine).

FIG. 6 is a view of ultraviolet and visible range absorption spectrum of zinc porphyrin polymer B-6 (in pyridine).

DETAILED DESCRIPTION OF THE INVENTION

First, a porphyrin array including, as a structural unit, bis(imidazolylporphyrin metal complex) or derivative thereof having an acetylenic bond for connecting the two imidazolylporphyrin metal complexes or derivatives thereof, exhibiting large two-photon absorption and represented by the formula (1-1) or (1-

2) will be described in detail.

Following description on the formula (1-1) will basically be applied to the formulas (1-2), (2), (3) and (4) as well, unless otherwise mentioned.

5 In the above-mentioned formula (1-1), M_1 represents an ion of metal which is capable of being the core metal of the porphyrin ring and forming a coordinate bond with the imidazolyl group represented by Im. Specific examples of the metal ion represented
10 by M_1 include Zn (II), Ga (III), Fe (II/III), Co (II/III), and Ru (II/III). However, the metal ion represented by M_1 is not limited to these, as long as the metal ion is capable of being the core metal of the porphyrin ring and forming a coordinate bond with the
15 imidazolyl group expressed as Im. Among the metal ions, Zn(II) is preferable in consideration of ease in the synthesis.

 In the formula (1-2), M_2 represents either two protons or an ion of metal which is incapable of
20 forming a coordinate bond with the imidazolyl group. Examples of the metal ion represented by M_2 include gold ion, nickel ion, and copper ion. However, the metal ion represented by M_2 is not limited to these. M_2 preferably represents two protons, in consideration
25 of ease in the synthesis.

 In the formula (1-1), R_1 represents a substituted or unsubstituted alkyl group, or substituted or

unsubstituted aryl group.

The substituted or unsubstituted alkyl group represented by R_1 includes normal, branched and cyclic alkyl groups.

5 The number of carbon atoms of the unsubstituted alkyl group or the alkyl moiety of the substituted alkyl group is not particularly limited as long as a porphyrin array represented by formula (1-1) can be formed. However, the number of carbon atoms of the
10 unsubstituted alkyl group or the alkyl moiety of the substituted alkyl group is preferably 1 to 20, and more preferably 2 to 20, in terms of ease in production, solubility and the like.

 In the case in which R_1 is a substituted alkyl
15 group, examples of the substituent include an alkoxy carbonyl group, an alkoxy group, an alkenoxy group, an alkenoxy carbonyl group and the like. However, the substituent is not limited to these examples.

 When R_1 is an alkoxy carbonyl alkyl group, the
20 number of carbon atoms of the alkoxy carbonyl moiety is not particularly limited as long as the porphyrin array can be formed. The number of carbon atoms of the alkoxy carbonyl moiety is generally in a range of 2 to 23. One example of the alkoxy carbonyl alkyl group
25 represented by R_1 is methoxycarbonyl ethyl.

 When R_1 is an alkoxy alkyl group, the number of carbon atoms of the alkoxy moiety is not particularly

limited as long as the porphyrin array can be formed. The number of carbon atoms of the alkoxy moiety is generally in a range of 1 to 22. One example of the alkoxyalkyl group represented by R_1 is ethoxypropyl.

5 When R_1 is an alkenoxyalkyl group, the number of carbon atoms of the alkenoxy moiety is not particularly limited as long as the porphyrin array can be formed. The number of carbon atoms of the alkenoxy moiety is generally in a range of 2 to 22. One example of the
10 alkenoxyalkyl group represented by R_1 is 2-propenoxypropyl.

 When R_1 is an alkenoxycarbonylalkyl group, the number of carbon atoms of the alkenoxycarbonyl moiety is not particularly restricted as long as the porphyrin
15 array can be formed. The number of carbon atoms of the alkenoxycarbonyl moiety is generally in a range of 3 to 24. One example of the alkenoxycarbonylalkyl group represented by R_1 is 2-propenoxycarbonylethyl.

 When R_1 is a carboxyalkyl group, one example of
20 the carboxyalkyl group is carboxyethyl.

 The substituted or unsubstituted aryl group represented by R_1 may be either monocyclic or in a form of fused rings.

 The number of carbon atoms of the unsubstituted
25 aryl group or the aryl moiety of the substituted aryl group is not particularly restricted as long as the porphyrin array can be formed. However, the number of

carbon atoms of the unsubstituted aryl group or the aryl moiety of the substituted aryl group is preferably 6 to 20, and more preferably 6 to 10, in terms of ease in production, solubility and the like. Examples of
5 the unsubstituted aryl group include phenyl, naphthyl, but the unsubstituted aryl group represented by R_1 is not limited to these.

When R_1 is a substituted aryl group, examples of the substituent include an alkyl group, alkoxy group,
10 alkoxy carbonyl group, alkenoxy group and alkenoxy carbonyl group. However, the substituent is not limited to these.

The number of carbon atoms of the alkyl group, alkoxy group, alkoxy carbonyl group, alkenoxy group, and
15 alkenoxy carbonyl group as the substituent of the substituted aryl group is the same as those defined in the above-mentioned those for R_1 . Examples of the alkylaryl group, alkoxyaryl group, alkoxy carbonylaryl group, alkenoxyaryl group and alkenoxy carbonylaryl
20 group represented by R_1 is, 4-methylphenyl, 4-methoxyphenyl, 4-(ethoxy carbonyl)-phenyl, 4-(2-propenoxy)-phenyl and 4-(2-propenoxy carbonyl)-phenyl, respectively. However the substituted aryl group is not limited to these.

25 In the formula (1-1), there exists a plurality of substituent groups R_1 . These R_1 groups may be the same or different. However, these groups are preferably the

same, in terms of ease in production. The same can be applied to each of the formulas (1-1), (1-2), (2), (3) and (4), when there exist a plurality of substituent groups represented by the same symbol.

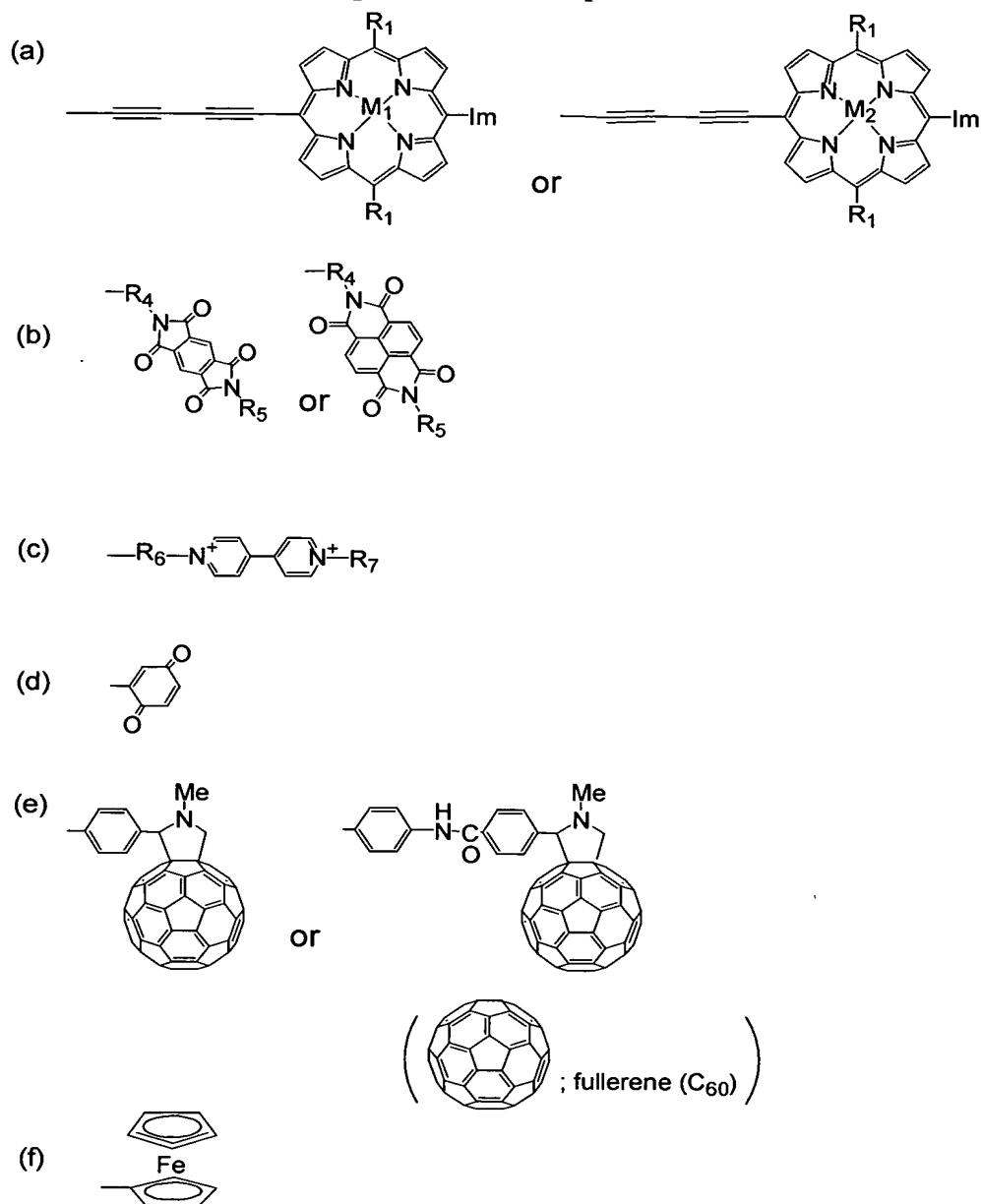
5 R₁ is preferably an alkyl group, alkyl-substituted aryl group or alkyloxy-substituted aryl group, in terms, e.g., of solubility of the resulting porphyrin array.

 When R₁ is a group having an olefin moiety, such as an alkenoxycarbonylalkyl group, alkenoxyalkyl group, 10 alkenoxyaryl group and alkenoxycarbonylaryl group, the group can be utilized in a cyclization metathesis reaction for producing a porphyrin array including, as a structural unit, bis(imidazolylporphyrin metal complex) fixed by covalent bonds and represented by the 15 formula (4) of the present invention, which will be described later.

 In the formula (1-1), R₂ and R₃ may be the same or different. Each of R₂ and R₃ represent a residue selected from the group consisting of: (a) a porphyrin 20 residue without a core metal or porphyrin complex residue having a core metal represented by M₁ or M₂ mentioned above, (b) a cyclic diimide residue, (c) a dialkylviologen residue, (d) a benzoquinone residue, (e) an N-methylpyrrolidine-fullerene derivative residue 25 and (f) a ferrocene residue.

 Specific examples of the residues (a) to (f) are as follows. However, the residues (a) to (f) are not

limited to these specific examples.



In the formulas, R₁, M₁, M₂ and Im have the same meaning as in formulas (1-1) and (1-2). R₄ and R₆ independently represent an alkylene group or arylene group. R₅ and R₇ independently represent an alkyl group, alkoxyalkyl group, alkoxy carbonyl group or aryl group. There is no specific preference of R₂ and R₃

among the residues (a) to (f), but the residue (d), benzoquinone, may be preferably used for ease in preparation.

5 The number of carbon atoms of the alkylene group and arylene group represented by R₄ and R₆ is not particularly limited, as long as these groups can constitute the terminal groups of the porphyrin array. The number of carbon atoms of the alkylene group and arylene group represented by R₄ and R₆ is preferably 1
10 to 20 (6 to 20 in the case of arylene group), and more preferably 2 to 20 (7 to 20 in the case of arylene group).

 The number of carbon atoms of the alkyl group and aryl group represented by R₅ and R₇ is not particularly
15 limited, as long as these groups can constitute the terminal groups of the porphyrin array. The number of carbon atoms of the alkyl group and aryl group represented by R₅ and R₇ is preferably 1 to 20 (6 to 20 in the case of aryl group), and more preferably 3 to 20
20 (7 to 20 in the case of aryl group).

 The number of carbon atoms of the alkoxyalkyl group and alkoxycarbonyl group represented by R₅ and R₇ is not particularly limited, as long as these groups can constitute the terminal groups of the porphyrin
25 array. The number of carbon atoms of the alkoxyalkyl group and alkoxycarbonyl group represented by R₅ and R₇ preferably 2 to 20, and more preferably 3 to 20.

The compounds which provide the residues (a) to (f) represented by R_2 and R_3 are commercially available or can be synthesized from other products which are commercially available by referring to documents.

5 In the formula (1-1), n represents an integer of 1 or more. The upper limit of n is not particularly restricted as long as the porphyrin array can be formed. It is assumed that synthesis of a porphyrin array is possible until n reaches, for example, approximately
10 1000.

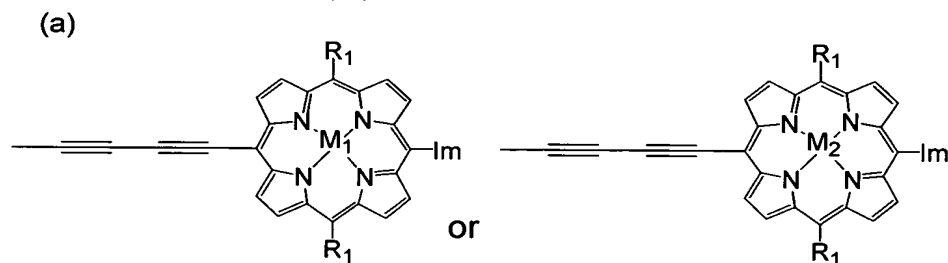
 In the formula (1-1), L_1 represents an acetylenic linking group represented by $(-C\equiv C-)_m$, wherein m represents an integer of 1 to 3. However, the polyacetylene group in which m exceeds 3 or any other
15 group may also be acceptable, as long as the porphyrin array represented by the formula (1-1) of the present invention exhibits large two-photon absorption.

 As shown in the formulas (1-1) and (1-2) of the present invention, in the imidazolylporphyrin dimer as
20 the structural unit, the imidazole ring of the imidazolyl group that bonds to each porphyrin of the dimer, is arranged so as to spread along a plane substantially perpendicular to a plane defined by the pyrrole rings and the methine groups. Further, the two
25 porphyrin rings are linked to each other with 1 to 3 acetylenic bond(s), so that the two porphyrin rings lie on the same plane. In the formulas (1-1) and (1-2),

each of the metals represented by M_1 , M_2 , M_3 and M_4 (except for the case in which M_2 , M_3 and M_4 are two protons) is bonded, by coordinate bond, to the nitrogen atom of the pyrrole nucleus surrounding the metal. Yet further, the core metal M_1 is bonded to the nitrogen atom of the imidazoly group by a coordinate bond.

Next, a porphyrin array including, as a structural unit, bis(imidazoly)porphyrin metal complex) and fixed by covalent bonds and represented by the formula (4) of the present invention (which porphyrin array will also be referred to as "the covalent bond-fixed porphyrin array of the present invention", hereinafter) will be described in detail.

The covalent bond-fixed porphyrin array of the present invention is a porphyrin array obtained by a cyclization metathesis reaction of the porphyrin array represented by the formula (1-1) of the present invention to fix the porphyrins by covalent bonds, wherein the terminal groups represented by R_2 and R_3 are the residue (a):

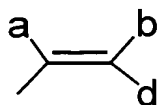


each having a core metal represented by M_1 or M_2 (wherein R_1 , M_1 , M_2 and Im have the same meaning as defined in the formula (1-1)); and at the same time,

the group represented by R₁ is a group having an olefin residue (i.e., alkenoxyalkyl group, alkenoxycarbonylalkyl group, alkenoxyaryl group or alkenoxycarbonylaryl group).

5 The covalent bond-fixed porphyrin array of the present invention exhibits large two-photon absorption, in a manner similar to the porphyrin arrays of the formulas (1-1) and (1-2). In the case of the porphyrin arrays represented by the formulas (1-1) and (1-2), the
10 coordinate bonds thereof tend to be cut off when the solvent to which the porphyrin arrays are dissolved has relatively high polarity. Therefore, the range in which the porphyrin arrays of the formulas (1-1) and (1-2) is applicable may be restricted, depending on the
15 available medium and the environment. On the contrary, in the covalent bond-fixed porphyrin array of the present invention, as fixation thereof is effected by covalent bonds, the degree of polymerization can be maintained in the stable manner without depending on
20 the polarity of the solvent to which the porphyrin array is dissolved, and thus the range in which the porphyrin arrays is applicable is widened, which is advantageous.

 In the formula (4), R represents an alkyl group or
25 a group represented by



wherein a, b and c independently represent H, an alkyl group or aryl group.

M_1 , L_1 and I_m have the same meaning as defined in the formula (1-1). M_3 has the same meaning as M_1 or M_2 .

5 p represents an integer of 1 or more, q represents an integer of 0 to 6, and r represents an integer of 0 to 4.

10 The alkyl group represented by R, a, b and c has the same meaning as the alkyl group mentioned above for R_1 of the formula (1-1).

15 p represents an integer of 1 or more. As is the case with n of the formula (1-1), the upper limit of p is not particularly restricted unless the formation of the porphyrin array is disturbed. It is assumed that synthesis of a porphyrin array is possible until p reaches, for example, approximately 1000.

20 q represents an integer of 0 to 6. q is preferably 2, in consideration of ease in the synthesis of the raw material compound thereof and functions which the resulting product is supposed to have.

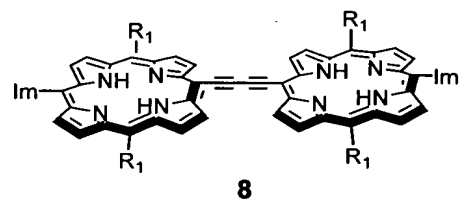
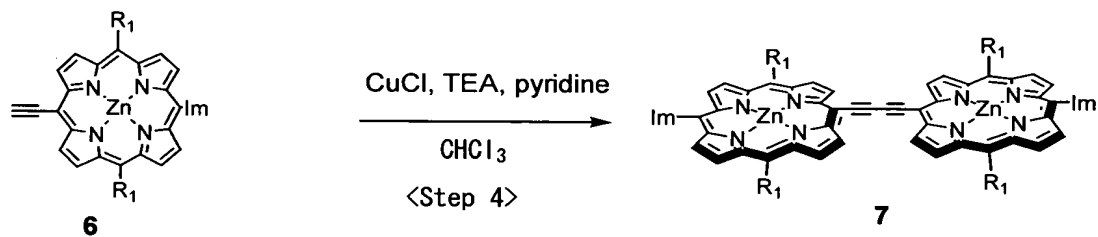
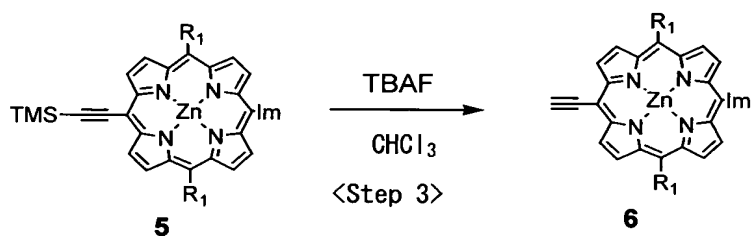
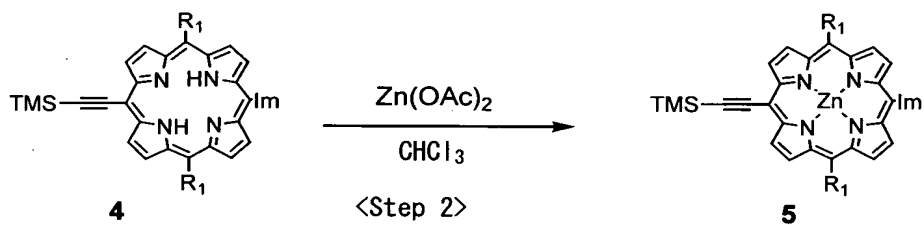
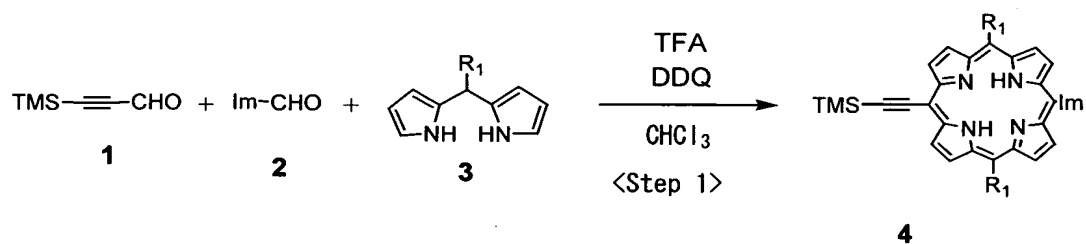
 r represents an integer of 0 to 4. r is preferably 1, in consideration of ease in the synthesis of the raw material compound thereof and functions which the resulting product is supposed to have.

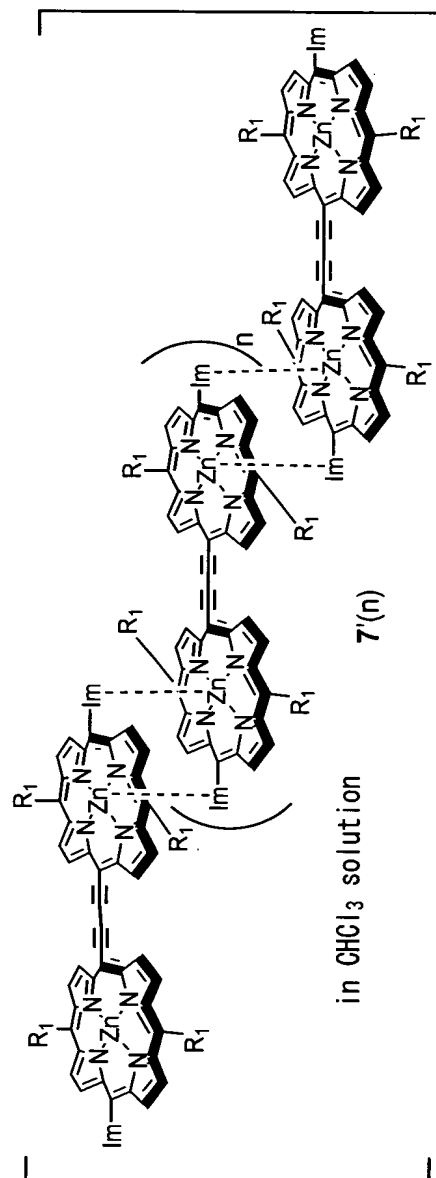
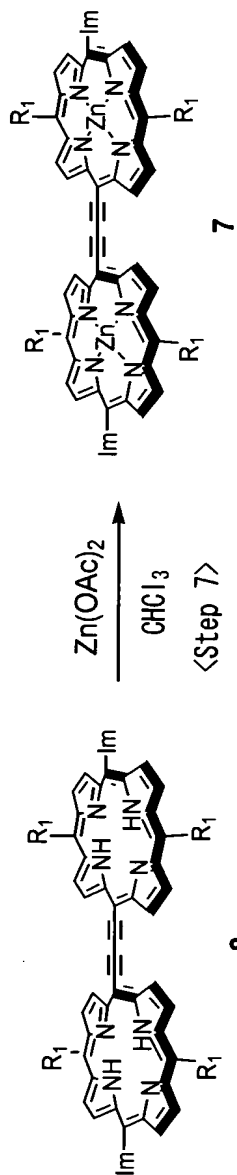
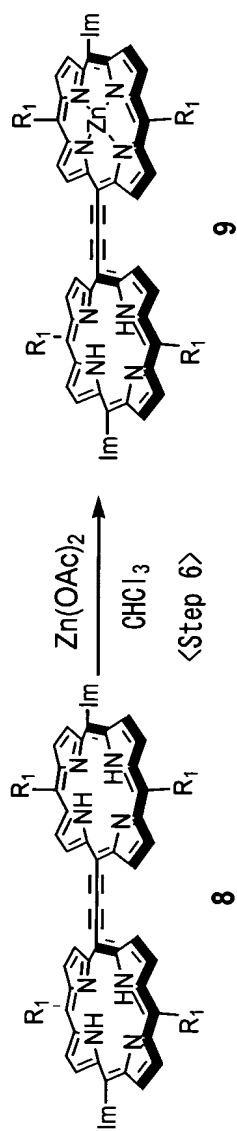
25 In the porphyrin array of the formula (4), the manner in which the porphyrin ring, the imidazolyl group and the core metal are bonded and configured with

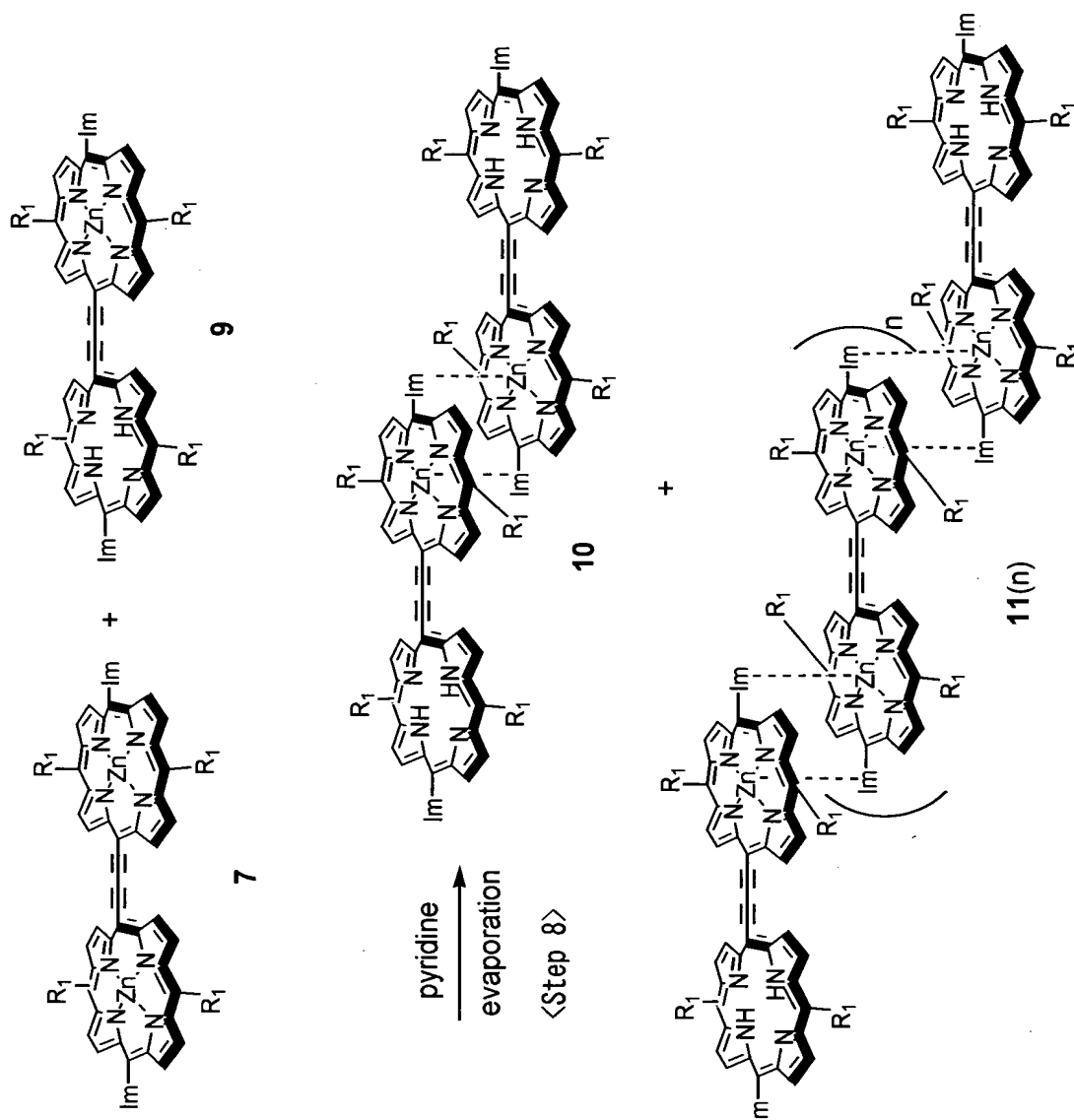
respect to each other is the same as that described in the formulas (1-1) and (1-2).

Hereinafter, there will be described a method of producing porphyrin arrays represented by the formula (1-1) wherein (i) both R_2 and R_3 are porphyrin zinc complex of residue (a), M_1 is Zn and L_1 is $(-C\equiv C-)_2$; and (ii) both R_2 and R_3 are free base porphyrin of residue (a), i.e., M_2 represents two protons, M_2 is Zn, L_1 is $(-C\equiv C-)_2$; and porphyrin arrays represented by the formula (1-2) wherein M_1 is Zn and M_2 represents two protons. Other porphyrin arrays of the present invention having other substituents may also be synthesized in a manner similar to this.

The porphyrin array of the present invention in which M_1 is Zn(II), and both R_2 and R_3 are free base porphyrins may be prepared by the following step 1 to step 8, but the preparation method is not limited to this.







<Step 1> Synthesis of compound 4

Compound 1 (wherein "TMS" represents

5 trimethylsilyl group), compound 2, compound 3 (in the
 formulas mentioned above, R₁ and Im have the same
 meaning as defined in the formulas (1-1) and (1-2), the
 same can be applied to the other compounds in the
 following description) are dissolved in a solvent such
 10 as CHCl₃ or acetonitrile and the atmosphere thereof is

substituted with nitrogen. Thereafter, TFA
(trifluoroacetic acid) is added to the mixture to start
the reaction. Chloranil (2,3,5,6-tetrachloro-p-
benzoquinone) is then added to the mixture, whereby
5 compound 4 is synthesized.

The ratio of the amounts to be added, of compound
1, compound 2 and compound 3, is generally set at 1:1:2
to 1:2:2.

The solvent may generally be used by the amount
10 which is 500 to 5000 times as much as the amount of
compound 2. The reaction temperature may generally be
set in a range of 20 to 30°C. The reaction time may
generally be set in a range of 30 to 300 minutes.

After the reaction is completed, processes such as
15 purification may optionally be carried out, and then,
the resulting substance is subjected to the next step,
step 2. The purification process may be carried out
after the reaction of step 1 is completed, for
example, by adding an aqueous solution of sodium
20 hydrogencarbonate to the resulting solution, then
adding a solvent such as chloroform or dichloromethane
thereto and separating the organic layer, concentrating
the separated organic layer to dryness, and thereafter
loading the obtained product on silica gel column
25 chromatography.

<Step 2> Synthesis of compound 5

Compound 4 obtained by the above-mentioned step 1

is converted into zinc complex 5. This reaction can be effected by dissolving compound 4 in a solvent such as chloroform or dichloromethane and adding zinc (II) acetate thereto.

5 The amount of zinc acetate to be added may generally be set at an amount which is 5 to 10,000 times as much as the amount of compound 4. The reaction temperature may generally be set at room temperature (in a range of around 25 to 30°C). The
10 reaction time may generally be set in a range of 0.5 to 3 hours.

 After the reaction is completed, the reaction solution may be washed with distilled water and the organic layer is concentrated under reduced pressure,
15 whereby compound 5 is obtained.

<Step 3> Synthesis of compound 6

 The TMS group of compound 5 obtained by the above-mentioned step 2 is removed. The removal of the TMS group can be effected by dissolving compound 5 in a
20 solvent such as chloroform or dichloromethane, and adding TBAF (tetrabutylammonium fluoride) thereto.

 The amount of TBAF to be added may generally be set at an amount which is 5 to 50 times as much as compound 5. The reaction temperature may generally be
25 set at room temperature. The reaction time may generally be set in a range of 1 to 6 hours.

 After the reaction is completed, the reaction

solution is washed with distilled water and the organic layer is concentrated under reduced pressure. The residue, compound 6, is subjected to the next step, step 4, without being purified.

5 <Step 4 and Step 5> Synthesis of compound 8

Compound 6 is dissolved in a solvent such as chloroform or dichloromethane. Pyridine is added to the mixture and then the mixture is stirred for 30 minutes. Thereafter, copper (I) chloride is added to
10 and reacted with the mixture at room temperature.

The addition amounts of compound 6, pyridine and copper (I) chloride are generally set in ratios of 1:1.5:10 to 1:3:200. The reaction temperature may generally be set at a temperature in a range of 20 to
15 30°C. The reaction time may generally be set in a range of 1 to 30 hours.

After the reaction is completed, the reaction solution is washed with an aqueous ammonia solution or an aqueous ethylenediamine solution, and the solvent of
20 the organic layer is evaporated off. The residue, compound 7, is dissolved in a solvent such as chloroform or dichloromethane, and *p*-TsOH (*p*-toluenesulfonic acid) is added thereto, thereby compound 8 is obtained.

25 The amount of *p*-TsOH to be added may generally be set at an amount of 2 to 100 times as much as compound 7. The reaction temperature may generally be set at

room temperature. The reaction time may generally be set in a range of 0.5 to 1 hour.

After the reaction is completed, the reaction solution is washed with distilled water and an aqueous sodium hydrogencarbonate solution and then the organic layer is concentrated under reduced pressure. The residue is purified with gel permeation chromatography (GPC) and silica gel chromatography, whereby compound 8 is obtained.

10 <Step 6> Synthesis of compound 9

One free base porphyrin of the bis(free base) porphyrins of compound 8 is converted into a zinc porphyrin. The conversion can be effected by dissolving compound 8 in a solvent such as chloroform or dichloromethane, and then adding zinc (II) acetate thereto.

The amount of zinc acetate to be added may generally be set at 1 to 2 times as much as compound 8. The reaction temperature may generally be set at room temperature. The reaction time may generally be set in a range of 0.5 to 3 hours.

After the reaction is completed, the reaction solution is washed with distilled water and then the organic layer is concentrated under reduced pressure. The resulting product is purified with GPC, whereby compound 9 is obtained. Compound 9 exist as compound 10 in chloroform.

<Step 7> Synthesis of compound 7 from compound 8

Both of the free base porphyrins of the bis(free base) porphyrin of compound 8 are converted into zinc porphyrins. The conversion can be effected by
5 dissolving compound 8 in a solvent such as chloroform or dichloromethane, and then adding zinc (II) acetate thereto.

The amount of zinc acetate to be added may generally be set at 5 to 10,000 times as much as
10 compound 8. The reaction temperature may generally be set at room temperature. The reaction time may generally be set in a range of 0.5 to 3 hours.

After the reaction is completed, the reaction solution is washed with distilled water and then the
15 organic layer is concentrated under reduced pressure. Compound 7 is in the form of bis-acetylen-type poly(porphyrin) in chloroform (compound 7' (n)).

<Step 8> Synthesis of porphyrin arrays, compound 10 and compound 11 (n)

20 Compound 7 and compound 9 are dissolved in pyridine and mixed with each other. The reaction temperature may generally be set at room temperature. The reaction time may be set at 0.5 hours. The solvent is removed under reduced pressure.

25 The mixture of compound 10 and compound 11 (n) may be separated by subjecting the mixture to GPC, and using a solvent such as chloroform as an eluent.

Polystyrene may generally be employed as a stationary phase in the column for purification with GPC.

The value of the repeating units (n) of compound 11 may be adjusted by changing the mixing ratio between compound 7 and compound 9. Specifically, the value of n of compound 11 is shifted to a larger value by increasing the mixing ratio of compound 7. Conversely, the value of n of compound 11 is shifted to a smaller value by increasing the mixing ratio of compound 9.

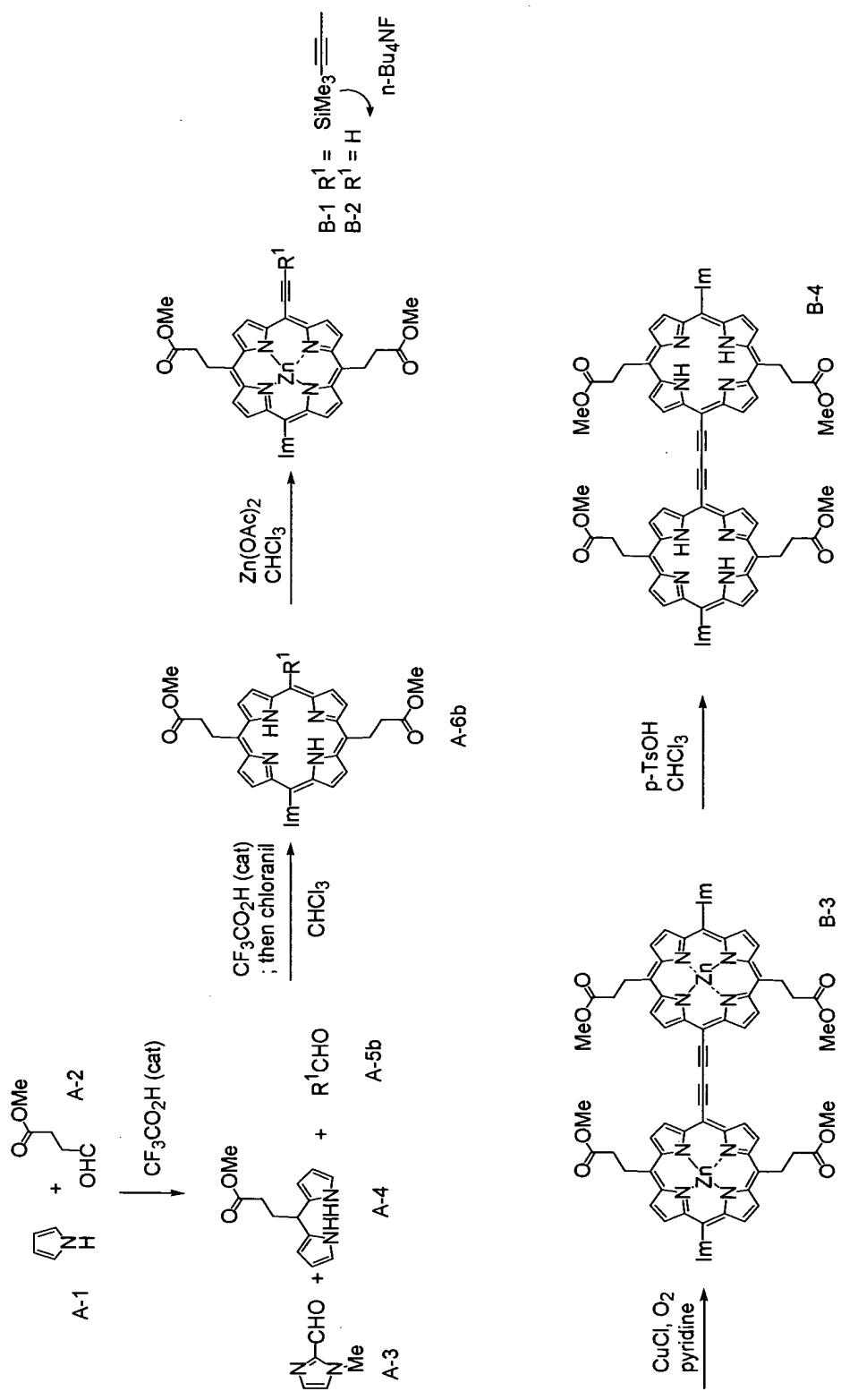
On the other hand, in the case of compound 7' (n) mentioned above, a non-polar solvent (such as chloroform, benzene and toluene) may be used in order to increase the value of n. Conversely, a polar solvent (such as methanol, ethanol and pyridine) may be used in order to decrease the value of n. A single solvent may be used, or a polar solvent and a non-polar solvent may be mixed in an appropriate manner, so that the polarity of the solvent as a whole can be adjusted as is desired.

Next, a method of preparing the covalent bond-fixed porphyrin array represented by the formula (4) of the present invention will be described by using an array wherein R is methyl, Im is 1-methyl-2-imidazolyl, $M_1=M_3$ =zinc ion, $L_1=(-C\equiv C-)_2$, $q=2$, $r=0$ and $a=H$ as an example. However, other covalent bond-fixed porphyrin arrays having different substituents may be synthesized in the similar manner as this.

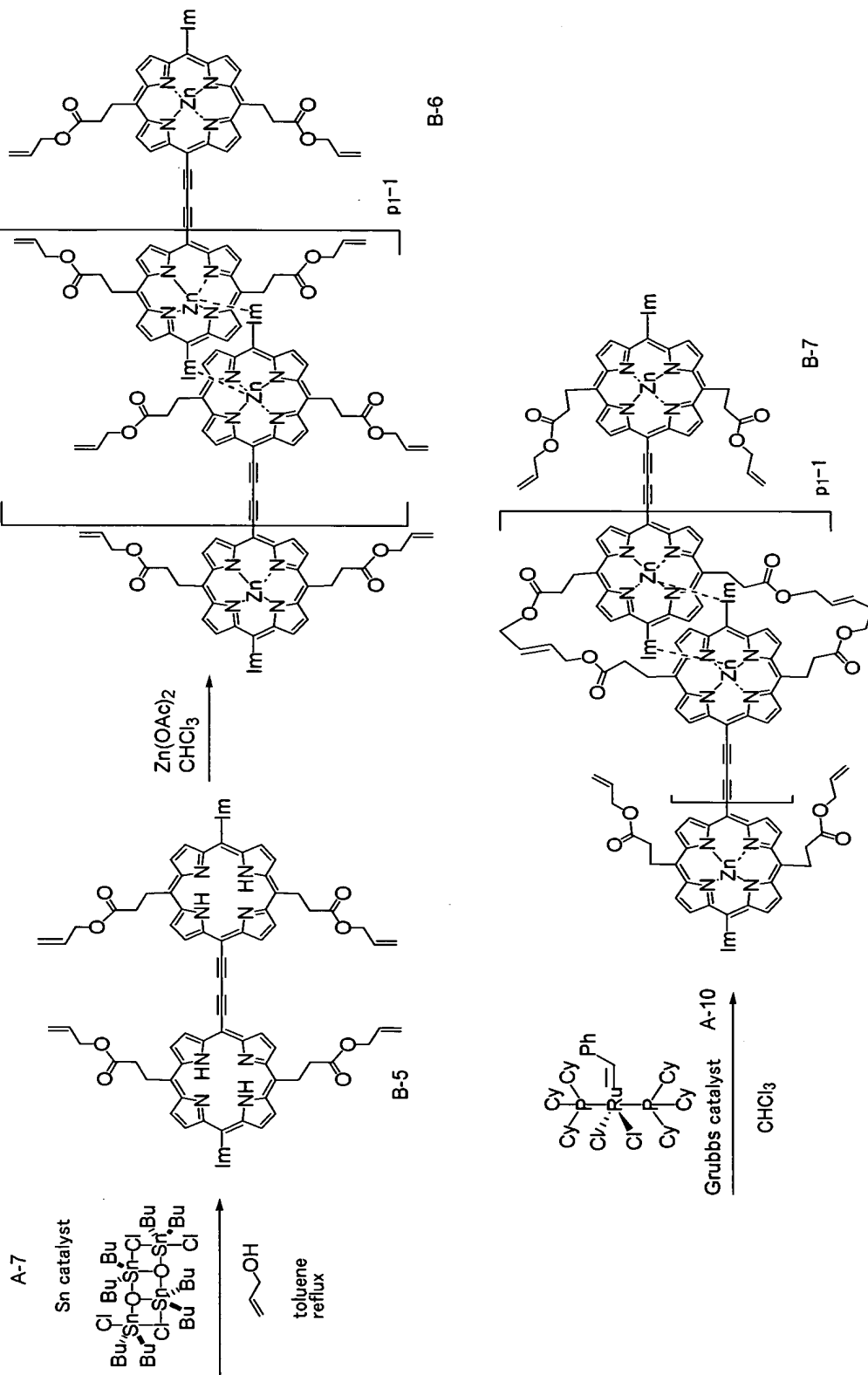
The covalent bond-fixed porphyrin array represented by the formula (4) wherein R is methyl, Im is 1-methyl-2-imidazolyl, $M_1=M_3$ =zinc ion, $L_1=(-C\equiv C-)_2$, $q=2$, $r=0$ and $a=H$ may be synthesized via the steps shown in the following scheme 1, but the preparation method thereof is not limited to this.

5

Scheme 1



Scheme 1 (continued)



By the above method, a mixtures of compounds represented by the formula (4) having different degrees of polymerization represented by p_1-1 is obtained. The mixture may be separated into each component having a single degree of polymerization by gel filtration column chromatogram and the like. The degree of polymerization represented by p_1-1 may be adjusted by changing the amounts of the intermediate, compound B-5, and Grubbs catalyst, and the reaction time.

The "Grubbs catalyst" herein is a generic term for the ruthenium carbene complex developed by Grubbs et al., which is reactive in the olefin metathesis reaction. When this complex is used, even if an olefin compound having various functional groups such as ester, ketone and amide is employed as a reaction substance, the reaction selectively proceeds only with respect to the olefin sites (refer to the general theory of Grubbs et al. (T. M. Trnka, R. H. Grubbs, Acc. Chem. Res. 34, 18 (2001), the entire contents of which is incorporated herein by reference).

Further, the reaction starting from compound B-6 to compound B-7 in Scheme 1 is a reaction known as the cyclization metathesis reaction, which is described in detail in the aforementioned reference by Grubbs et al.

The cyclization metathesis reaction is, in short, a reaction in which a compound having two alkenyl groups causes an olefin metathesis reaction to forms a cyclic

compound.

The group represented by R of the both terminal porphyrins of compound B-6 and compound B-7 has the same meaning as defined for the substituent, R, in the formula (4). Typical examples of R include $-\text{CH}=\text{CH}_2$.

Examples

<Example 1>

An example of synthesizing the porphyrin arrays represented by the formulas (1-1) and (1-2) of the present invention will be described hereinafter. It should be noted that the method of synthesizing the porphyrin arrays of the present invention is not restricted to the present example.

1) Step 1

Synthesis of 5,15-bis(heptyl)-10-(trimethylsilyl-propargyl)-20-(1-methyl-2-imidazolyl)porphyrin (4)

1g (4.1 mmol) of Meso-(n-heptyl)dipyromethane, 450 mg (4.1 mmol) of 1-methyl-2-formylimidoazole, 260 mg (2 mmol) of 1-trimethylsilylethynylaldehyde were added to 1 L of chloroform. The atmosphere of the reaction solution was substituted with N_2 . Then, 1.2 mL (8.6 mmol) of trifluoroacetic acid was added to the reaction mixture. After the reaction mixture was stirred for 4 hours at room temperature, 1.6g (6.5 mmol) of 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) was added thereto. The reaction solution was then stirred for 3 hours. Thereafter, an aqueous

solution of saturated sodium hydrogencarbonate was added to the mixture and the organic layer was extracted with chloroform. The extracted organic layer was dried with anhydrous sodium sulfate, and then the solvent was evaporated under reduced pressure. The obtained crude product was subjected to separation with silica gel chromatography (eluent: chloroform/acetone (9:1)), whereby 56 mg of the pure porphyrin 4 was obtained (the yield was 4%).

^1H NMR (600 MHz, CDCl_3) δ -2.71 (s, 2H; inner proton), 0.52 (s, 9H; TMS), 0.73 (t, $J = 7$ Hz, 6H; C7), 1.14-1.16 (m, 8H; C6, C5), 1.29-1.34 (m, 4H, C4), 1.54 (quintet, 4H; C3), 2.20-2.22 (m, 4H; C2), 3.12 (s, 3H; NCH_3), 4.40-4.48 (m, 4H; C1), 7.30 (s, 1H; imidazole ring), 7.57 (s, 1H; imidazole ring), 8.20 (br, 2H, β), 8.91 (br, 2H, β), 9.16 (d, $J = 4$ Hz, 2H, β), 9.55 (d, $J = 4$ Hz, 2H, β); ^{13}C NMR (150 MHz, CDCl_3) δ 0.50 (TMS), 14.2 (C7), 22.8 (C6), 29.4 (C4), 30.5 (C3), 32.0 (C5), 34.6 (NCH_3), 34.9 (C1), 38.7 (C2), 100.0 (TMS- $\text{C}\equiv\text{C}$ -), 102.2 (meso), 107.5 (TMS- $\text{C}\equiv\text{C}$ -), 114.8 (meso), 119.1 (meso), 121.4 (imidazole ring), 126.3 (imidazole), 127-131 (br, 4 carbons ($\text{Por}\beta$ 1-4)), 144-148 (br, 4 carbons (α 1-4)), 148.2 (imidazole), Other 4 carbons ($\text{Por}\alpha$) could not observed by
boarding.; UV (CHCl_3) : 667 (Abs.; 0.0061), 608 (0.0028), 567 (0.0108), 528 (0.0072), 427 (0.1950) nm; Fluorescence (EX = 427 nm, CHCl_3) : 741, 670 nm;

MALDI-TOF Mass $C_{43}H_{54}N_6Si$ Calcd: 682.42; Found: 683.1
(M+H)⁺.

2) Step 2

Synthesis of 5,15-bis(heptyl)-10-(trimethylsilyl-
5 propargyl)-20-(1-methyl-2-imidazolyl)porphyrin zinc
complex (5)

3 mL of a methanol solution of saturated zinc
acetate was added to a chloroform solution (12 mL) of
the porphyrin 4 (40 mg, 58.6 μ mol). The reaction
10 mixture was stirred for 1 hour at room temperature.
Thereafter, water was added to the reaction mixture and
the organic layer was extracted with chloroform. The
extracted organic layer was dried with anhydrous sodium
sulfate and then the solvent was evaporated under
15 reduced pressure, whereby 44 mg of the pure porphyrin
complex 5 was obtained (yield: 100%).

¹H NMR (600 MHz, CDCl₃) δ 0.73 (s, 9H; TMS), 1.00
(t, J = 7 Hz, 6H; C7), 1.44-2.49 (m, 4H; C6, C5),
1.50-1.57 (m, 4H, C6, C5), 1.65 (s, 3H; NCH₃),
20 1.94-1.99 (m, 2H, C3), 2.04 (d, J = 2 Hz, 1H; imidazole
ring), 2.00-2.07 (m, 2H; C3), 2.70-2.74 (m, 2H; C2),
2.85-2.89 (m, 2H; C2), 4.96-5.09 (m, 4H, C1), 5.38
(d, J = 4 Hz, 2H; Por β), 5.47 (d, J = 2 Hz, 1H;
imidazole ring), 8.81 (d, J = 4 Hz, 2H; Por β), 9.61
25 (d, J = 4 Hz, 2H; Por β), 9.91 (d, J = 4 Hz, 2H; Por β);
¹³C NMR (150 MHz, CDCl₃) δ 0.7 (TMS), 14.3 (C7), 22.9
(C6), 29.8 (C4), 31.0 (C3), 32.3 (C5), 32.7 (NCH₃),

35.9 (C1), 39.5 (C2), 98.4 (*meso*), 99.0 (TMS-C≡C-),
99.7 (TMS-C≡C-), 109.7 (*meso*), 117.9 (imidazole ring),
118.9 (*meso*), 121.4 (imidazole ring), 127.3 (Porβ4),
129.0 (Porβ1), 129.3 (Porβ3), 131.3 (Porβ2), 145.5
5 (imidazole), 147.4 (Porα), 150.2 (Porα), 150.8 (Porα),
151.6 (Porα); UV (CHCl₃) : 642 (Abs.; 0.0270), 577
(0.0090), 444 (0.1839), 425 (0.1136) nm; Fluorescence
(EX = 444 nm, CHCl₃) : 704, 645 nm; MALDI-TOF Mass
C₄₃H₅₂N₆SiZn Calcd: 744.33; Found: 745.2 (M+H)⁺.

10 3) Step 3

Synthesis of 5,15-bis(heptyl)-10-ethynyl-20-(1-methyl-
2-imidazolyl)porphyrin zinc complex (6)

1 M TBAF solution dissolved in THF (0.18 mL, the
TBAF content being 0.18 mmol) was added to a chloroform
15 solution (5 mL) of the porphyrin complex 5 (44 mg,
59 μmol) under a nitrogen atmosphere. The reaction
mixture was stirred for 1 hour at room temperature.
Thereafter, water was added to the reaction mixture and
the organic layer was extracted with chloroform. The
20 extracted organic layer was dried with anhydrous sodium
sulfate and then the solvent was evaporated under
reduced pressure, whereby 40 mg of the pure porphyrin
complex 6 was obtained.

UV-vis (CHCl₃) : 636 (Abs. 0.0806), 576 (0.0393), 440
25 (0.7057), 422 (0.4889) nm; Fluorescence (EX = 440 nm,
CHCl₃) : 698, 640 nm; MALDI-TOF Mass C₄₀H₄₄N₆O₄Zn
Calcd: 672.29; Found: 673.4 (M+H)⁺.

4) Step 4 and Step 5

Synthesis of 1,3-bis(5-(15-(1-methyl-2-imidazolyl)-10,20-bis(heptyl)-porphyrinyl)) butadiyne (8)

1.9g of copper (I) chloride (18.9 mmol) was added
5 to a pyridine solution (20 mL) of porphyrin complex 6
(180 mg, 0.27 mmol), and oxygen was vigorously blown
into the solution. The reaction mixture was stirred
for 2 hours at room temperature and then washed with
25% aqueous solution of ammonia. The organic layer was
10 extracted with chloroform. The extracted organic layer
was dried with anhydrous sodium sulfate and then the
solvent was evaporated under reduced pressure. The
obtained crude product of the desired zinc complex 7
was dissolved in chloroform (10 mL), and *p*-
15 toluenesulphonic acid monohydrate (27 mmol) was added
thereto. The reaction mixture was stirred for 1 hour
at room temperature. Thereafter, an aqueous solution
of saturated sodium hydrogencarbonate was added to the
reaction solution to neutralize the reaction solution.
20 The crude product was extracted with chloroform. The
obtained crude product was purified with silica gel
chromatography (eluent: chloroform/methanol (10: 1)),
whereby 50 mg of the desired product 8 was obtained at
the yield of 15%.
25 UV-vis (CHCl₃) : 715 (Abs. 0.0854), 609 (0.0648), 475
(0.2000), 444 (0.3149) nm; Fluorescence (EX = 444 nm,
CHCl₃) : 800, 721 nm; MALDI-TOF Mass C₈₀H₉₀N₁₂ Calcd:

1218.74; Found: 1219.5 (M+H)⁺.

5) Step 6

Synthesis of 1-(5-(15-(1-methyl-2-imidazolyl)-10,20-bis(heptyl)-zinc porphyrinyl))-3-(5'-(15'-(1-methyl-2-imidazolyl)-10',20'-bis(heptyl)-porphyrinyl)) butadiyne (9)

A methanol solution of zinc acetate (0.9 mg/0.5 mL, 4 μ mol) was added to a chloroform solution (2 mL) of the bis-porphyrin 8 (5 mg, 4 μ mol). The reaction mixture was stirred for 1 hour. Thereafter, water was added to the reaction mixture and the organic layer was extracted with chloroform. The extracted organic layer was dried with anhydrous sodium sulfate and then the solvent was evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (eluent: chloroform/methanol (10: 1)), whereby 5.5 mg of the desired product 9 was obtained with an equivalent amount. The porphyrin mono-complex 9 exists as a coordinated assembly 10 in chloroform. UV-Vis (CHCl₃) : 732 (Abs.; 0.3639), 660 (0.1328), 583 (0.1194), 484 (0.7188), 455 (0.6266), 429 (0.6525) nm; Fluorescence (EX = 484 nm, CHCl₃) : 840, 749 nm; MALDI-TOF Mass C₈₀H₈₈N₁₂Zn₁ Calcd: 1280.65; Found: 1281.7 (M+H)⁺.

6) Step 7

Synthesis of 1,3-bis(5-(15-(1-methyl-2-imidazolyl)-10,20-bis(heptyl)-zinc porphyrinyl)) butadiyne (7)

3 mL of a methanol solution of saturated zinc acetate was added to a chloroform solution (3 mL) of the porphyrin 8 (10 mg, 8 μ mol). The reaction mixture was stirred for 1 hour at room temperature. Thereafter, water was added to the reaction mixture and the organic layer was extracted with chloroform. The extracted organic layer was dried with anhydrous sodium sulfate and then the solvent was evaporated under reduced pressure, whereby 11 mg of the porphyrin complex 7 was obtained at the yield was 100%.

UV-Vis (CHCl_3) : 732 (Abs.; 0.3639), 660 (0.1328), 583 (0.1194), 499 (0.7188), 455 (0.6266), 429 (0.6525) nm; Fluorescence (EX = 484 nm, CHCl_3) : 840, 749 nm; MALDI-TOF Mass $\text{C}_{80}\text{H}_{88}\text{N}_{12}\text{Zn}_2$ Calcd: 1348.65; Found: 1349.7 (M+H)⁺.

7) Step 8

Synthesis of porphyrin array (11)

2.5 μ mol of the porphyrin complex 7 and 7.7 μ mol of the porphyrin mono-complex 9 were dissolved in 3 mL of pyridine. The mixture was stirred for 30 minutes at room temperature. The solvent was removed by a vacuum pump, whereby a mixture of the array 10 and the array 11 (n) were obtained.

<Measurement example 1>

8) Measurement of two-photon absorption cross section

The spectra of two-photon absorption of the arrays were measured in a chloroform solution, using the open

aperture Z-scan method, with a Ti: sapphire pulse laser having a time resolution of 120 femtosecond. The wavelength was varied from 817 to 1282 nm by an optical parametric amplifier (OPA). The measurement was
 5 carried out using a 1 mm cell and scanning a distance of 60 mm fore and aft of the focus of the incident light (below 1 mW). No change was observed in the visible and ultraviolet absorption spectrum between before and after the Z-scan measurement. The value of
 10 the two-photon absorption cross section $\sigma^{(2)}$ was obtained from the following formula.

$$\sigma^{(2)} = h\omega\beta/N \quad (1)$$

In the above-mentioned formula (1), $h\omega$ represents photon energy, N represents the number density of
 15 molecules, β represents the two-photon absorption coefficient, satisfying the following formula.

$$q = \beta I_0 L \quad (2)$$

In the above-mentioned formula (2), the parameter q corresponds to the two-photon absorbance and can be
 20 obtained by performing "fitting" of the open aperture Z-scan curve with the theoretical equations (3) and (4) below. I_0 represents intensity of the incident light (IEEE. J. Quant. Electron. 26, 760, (1990), Handbook of Nonlinear Optics, Marcel Dekker, New York (1996)).

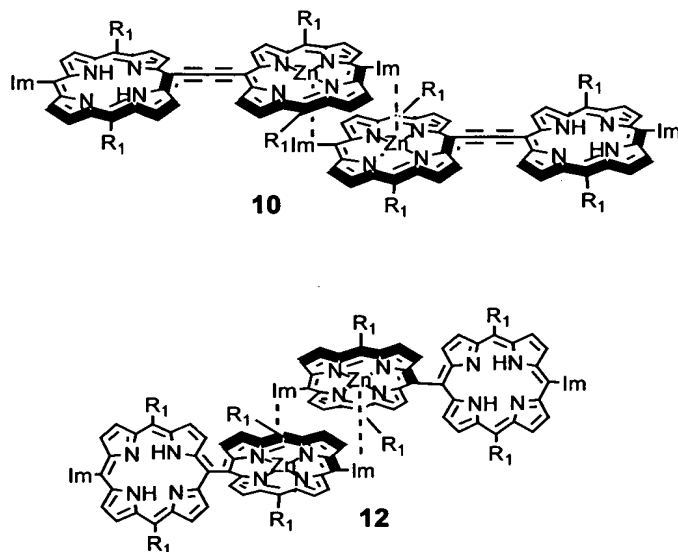
25

$$T(\zeta) = \frac{(1-R)^2 e^{(-\alpha^{(1)}L)}}{\sqrt{\pi q(\zeta)}} \int_{-\infty}^{\infty} \ln[1 + q(\zeta)e^{(-x^2)}] dx \quad (3)$$

$$q(\zeta) = \frac{q}{1 + \zeta^2} \quad (4)$$

Equation (3) describes the normalized transmittance of a sample that exhibits only two-photon absorption as nonlinear absorption for a Gaussian-pulsed Gaussian beam, where ζ is the normalized z-position defined as $\zeta = (z - z_0)/z_R$ and z_0 and z_R are the focal position and the Rayleigh range, respectively. $T(\zeta)$ is normalized to unity at a position far from the focal position, i.e., $T(\zeta \rightarrow \pm\infty) = 1$. $\alpha^{(1)}$ is the linear (one-photon) absorption coefficient, R is Fresnel reflectance at the curvette cell walls, and L denotes the path length of the sample.

FIG. 1 shows the two-photon absorption spectrum of the array 10 and that of reference array 12 measured by the above-mentioned method. Another, smaller graph marked by the black arrow in FIG. 1 shows the spectrum of reference array 12 which has been enlarged in the direction of the vertical axis thereof. The structures of the array 10 and reference array 12 are shown below.



(wherein R_1 = n-heptyl and Im = 1-methyl-2-imidazolyl).

The method of synthesizing reference array 12 has already been reported (J. Am. Chem. Soc., 124, 22-23 (2002)). Reference array 12 includes meso-type dimer of mono-zinc complexes, and is in an assembled structure formed by coordinate bonds, in chloroform, as shown in FIG. 1.

The vertical axis of the spectra represents two-photon absorption cross section $\sigma^{(2)}$, and the unit thereof, i.e., 1 GM, corresponds to $1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$. The maximum value of the two-photon absorption cross section of the reference array 12, which is of meso-type, was 370 GM (at 964 nm). On the contrary, the maximum value of the two-photon absorption section of the array 10, which was of bis-acetylen-type, was 7600 GM (at 887 nm), which was approximately 20 times as much as the maximum value of the two-photon absorption cross section of the

reference array 12. It is assumed that the conjugation system between the porphyrins of the bis-acetylen-type is expanded and thus the molecular polarization therein due to the absorption of the first photon becomes
5 larger than that observed in the meso-type, whereby the transition probability of the absorption of the second photon, of the bis-acetylen-type, is increased, as compared with the meso-type.

In the measurement using a femtosecond laser,
10 there have been very few reports in which the maximum value of the two-photon absorption cross section reached 1000 GM. In 2002, Drobizhev et al. reported that octanitrophenyltetraazaporphyrin having
15 nitrophenyl groups as acceptors exhibits 1600 GM (at 770 nm, 150 fs) (Chem. Phys. Lett., 361, 504-512 (2002)). However, it is generally difficult, in terms of organic synthesis, to introduce an acceptor by a covalent bond. Conversely, in the present invention, coordinate bonds are used and thus, an acceptor/donor
20 can be easily introduced to the porphyrin array. It has been discovered by using ultrafast femtosecond laser that the porphyrin array of the present invention exhibits large two-photon absorption.

The two-photon absorption cross sections of the
25 porphyrin array 10 of the invention and reference array 12 are summarized in Table 1 below.

Table 1

Sample	σ (2)/GM	σ (2)/GM (per porphyrin)	Wavelength/nm
10	7600	1900	887
12	370	91	964

<Example 2>

A synthesis example of the porphyrin array represented by the formula (4) of the present invention will be described below, but the synthesis method thereof is not limited to this.

Meso-(methoxycarbonylethyl)dipyrromethane (A-4)

Meso-(methoxycarbonylethyl) dipyrromethane (A-4) was synthesized by stirring methoxycarbonyl propanal (11.6 g, 0.1 mol) and pyrrole (280 mL, 4 mol) in the presence of trifluoroacetic acid (1.4 mL, 10 mmol), in a method similar to that described in the reference (Y. Tomohiro, A. Satake, Y. Kobuke, J. Org. Chem. 2001, 66, 8442-8446). The resulting product was purified with silica gel chromatography (eluent: hexane/EtOAc (5:1)), whereby 17 g (73%) of meso-(methoxycarbonylethyl) dipyrromethane (A-4) was obtained.

^1H NMR (600 MHz, CDCl_3) δ 2.22-2.26 (m, 2H), 2.29-2.33 (m, 2H), 3.63 (s, 3H), 3.99 (t, $J = 7.2$ Hz, 1H), 6.05-6.07 (m, 2H, pyH4), 6.12-6.14 (m, 2H, pyH5), 6.58--6.62 (m, 2H, pyH2), 7.78 (br, 2H, NH); ^{13}C NMR (150 MHz, CDCl_3) δ 29.5, 31.9, 36.9, 51.6, 105.8,

108.1, 117.3, 132.4, 174.0.

Sn catalyst A-7

Sn catalyst A-7 was synthesized according to the method of Otera et al. and used for the present example
5 (Junzo Otera, Nobuhisa Dan-oh, Hitosi Nozaki, J. Org. Chem. 1991, 56, 5307-5311).

Grubbs catalyst A-10

Fluka 09587 (manufactured by Fluka Co., Ltd.)
(Benzylidene-bis(tricyclohexylphosphine)-
10 dichlororuthenium) was purchased from WAKENYAKU Co., Ltd, and used for the present example.

5,15-Bis(methoxycarbonylethyl)-10-(1'-trimethylsilylethynyl)-20-(1''-methyl-2''-imidazolyl)porphyrin (A-6b)

15 This compound was prepared by adding *meso*-(methoxycarbonylethyl)dipyrromethane A-4 (3 g, 13 mmol), 1-methyl-2-formyl-imidazole A-3 (1.4 g, 13 mmol), 1-trimethylsilyl-ethynylaldehyde A-5b (0.8 g, 6.5 mmol), trifluoroacetic acid (3.7 mL, 26 mmol) and chloranil
20 (4.8 g, 20 mmol), to deoxygenated chloroform (3 L). The thus obtained crude product was loaded on a silica gel column chromatography (eluent: chloroform / MeOH (9 : 1)) to give A-6b (120 mg, 3%).

¹H NMR (600 MHz, CDCl₃) δ -2.78 (s, 2H; inner proton),
25 0.67 (s, 9H; TMS), 3.33 (s, 3H; NCH₃), 3.43 (t, *J* = 7.2 Hz, 4H; ester β), 3.7 (s, 6H; COOMe), 5.17-5.19 (m, 4H; ester α), 7.46 (br.s, 1H; imidazole ring),

7.70 (br.s, 1H; imidazole ring), 8.71 (d, $J = 4.2$ Hz, 2H; Por β), 9.34 (d, $J = 4.2$ Hz, 2H; Por β), 9.41 (d, $J = 4.2$ Hz, 2H; Por β), 9.70 (d, $J = 4.2$ Hz, 2H; Por β); ^{13}C NMR (150 MHz, CDCl_3) δ 0.4 (TMS), 30.2 (ester α), 34.6 (NCH $_3$), 41.7 (ester β), 52.0 (COOMe), 100.1 (TMS-C \equiv C-), 102.5 (meso), 106.4 (meso), 107.1 (TMS-C \equiv C-), 118.3 (meso), 121.7 (imidazole ring), 128.2 (Por β), 128.3 (imidazole ring), 128.4 (Por β), 131.2 (Por β), 131.9 (Por β), 144-147 (br, 4 carbons (Por α)), 148.4 (Im N-C=N), 173.0 (C=O); UV-Vis (CHCl_3) : 665 (Abs.; 0.0651), 608 (0.0553), 566 (0.1405), 527 (0.1086), 427 (2.3982) nm; Fluorescence (EX = 427 nm, CHCl_3) : 740, 668 nm; MALDI-TOF MASS $\text{C}_{37}\text{H}_{38}\text{N}_6\text{O}_4\text{Si}$ Calcd: 658.27; Found: 659.2 (M+H) $^+$.
5,15-Bis(methoxycarbonylethyl)-10-(1'-trimethylsilylethynyl)-20-(1''-methyl-2''-imidazolyl)porphyrinatozinc (B-1)

To a chloroform solution (15 mL) of porphyrin A-6b (120 mg, 0.18 mmol), a methanol solution (5 mL) of saturated zinc acetate was added. After stirring the mixture for 1 hour at room temperature, water was added to the reaction solution, and the organic layer was extracted with chloroform. The extracted organic layer was dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure, thereby 130 mg of B-1 was obtained.

^1H NMR (600 MHz, CDCl_3) δ 0.74 (s, 9H; TMS), 1.65 (s,

3H; NCH₃), 1.98 (br.s, 1H; imidazole ring), 3.64-3.81 (m, 4H; ester β), 3.89 (s, 6H; COOMe), 5.42-5.53 (m, 7H; ester α & imidazole ring & Por β 4), 8.86 (d, J = 5 Hz, 2H; Por β 3), 9.66 (d, J = 5 Hz, 2H; Por β 1), 9.93 (d, J = 5 Hz, 2H; Por β 2); ¹³C NMR (150 MHz, CDCl₃) δ 0.7 (TMS), 31.0 (ester α), 32.7 (NCH₃), 42.5 (ester β), 52.1 (COOMe), 98.7 (meso), 99.8 (TMS-C \equiv C-), 100.4 (TMS-C \equiv C-), 109.2 (meso), 118.4 (imidazole ring), 118.5 (meso), 121.9 (imidazole ring), 127.9 (Por β 4), 128.8 (Por β 1), 129.3 (Por β 3), 131.9 (Por β 2), 145.5 (Im N-C=N), 147.7 (Por α), 150.0 (Por α), 150.5 (Por α), 152.0 (Por α), 172.6 (C=O).

5,15-Bis(methoxycarbonyl)ethyl)-10-(ethynyl)-20-(1'-methyl-2'-imidazolyl)porphyrinatozinc (B-2)

To a chloroform solution (15 mL) of porphyrin B-1 (130 mg, 0.18 mmol), 1M THF solution of tetrabutylammonium fluoride (0.6 mL) was added. After stirring the mixture for 30 min at room temperature, water was added to the reaction solution, and the organic layer was extracted with chloroform. The extracted organic layer was dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure, thereby 117 mg of B-2 was obtained

¹H NMR (600 MHz, CDCl₃) δ 1.66 (s, 3H; NCH₃), 2.0 (d, J = 1.2 Hz, 1H; imidazole ring), 3.61-3.82 (m, 4H; ester β), 3.90 (s, 6H; COOMe), 5.42-5.45 (m, 4H; ester α), 5.45 (d, J = 4.2 Hz, 2H; Por β 4), 5.55 (d, J = 1.2

Hz, 1H; imidazole ring), 8.87 (d, $J = 4.2$ Hz, 2H; $\text{Por}\beta$ 3), 9.67 (d, $J = 4.2$ Hz, 2H; $\text{Por}\beta$ 1), 9.95 (d, $J = 4.2$ Hz, 2H; $\text{Por}\beta$ 2); UV (CHCl_3) : 632 (Abs. 0.0125), 576 (0.0087), 440 (0.1280), 422 (0.0874) nm; Fluorescence (EX = 440 nm, CHCl_3) : 694, 634, (EX = 422 nm, CHCl_3) : 691, 635 nm; MALDI-TOF Mass $\text{C}_{34}\text{H}_{28}\text{N}_6\text{O}_4\text{Zn}$ Calcd: 648.15; Found: 649.12 ($\text{M}+\text{H}$)⁺.

1,4-Bis[10{5',15'-Bis(methoxycarbonylethyl)-20'-(1"-methyl-2"-imidazolyl)porphyrinyl}]ethan-1,3-diyne (B-4)

10 Cuprous chloride (89 mg) was added to porphyrin B-2 (117 mg, 0.18 mmol) in pyridine (20 mL). The reaction solution was stirred for 1 hour at room temperature under oxygen gas bubbling. Thereafter, water was added to the reaction solution, and extracted
15 with chloroform. The extracted organic layer was washed with a saturated EDTA (ethylenediamine tetraacetic acid) aqueous solution and dried over anhydrous sodium sulfate, and then the solvent was evaporated under reduced pressure. An excessive amount
20 of p-toluenesulphonic acid monohydrate was added to a chloroform solution (10 mL) of the thus obtained crude product, and the mixture was stirred for 1 hour. Thereafter, an aqueous solution of saturated sodium hydrogencarbonate was added to the mixture. The
25 organic layer was extracted with chloroform. The extracted organic layer was dried over anhydrous sodium sulfate, and then the solvent was evaporated under

reduced pressure. The thus obtained crude product was loaded on a silica gel column (eluent:

chloroform/methanol (9 : 1)) to give B-4 (84 mg, 40%).

MALDI-TOF MASS $C_{68}H_{58}N_{12}O_8$ Calcd: 1170.45; Found:

5 1171.33 (M+H)⁺.

1,4-Bis[10{5',15'-Bis(allyloxycarbonylethyl)-20'-(1"-methyl-2"-imidazolyl)porphyrinyl}]ethan-1,3-diyne (B-5)

10 Porphyrin B-4 (80 mg, 68 μ mol) and allyl alcohol (93 μ L, 1.4 mmol) in toluene (1 mL) was stirred under N₂ atmosphere. Thereafter, the Sn catalyst A-7 (1 mg, 2 μ mol) was added to the solution, and solution was refluxed for 4 hr at 120°C. The completion of the reaction was checked with MALDI-TOF MASS. Thereafter, water was added to the reaction solution, and extracted
15 the organic layer with chloroform. The extracted organic layer was dried over anhydrous sodium sulfate and then the solvent was evaporated under reduced pressure to obtain crude product. The thus obtained crude product was loaded on a silica gel chromatography
20 (eluent: chloroform/methanol (10 : 1)), to give pure B-5 (64 mg, 80%).

¹H NMR (600 MHz, CDCl₃) δ -2.82 (s, 4H; inner proton), 3.34 (br.s, 6H; NCH₃), 3.42-3.48 (m, 8H; ester β), 4.68-4.71 (m, 8H; O-CH₂-C=C), 4.94-5.08 (m, 8H; ester α), 5.23 (br.d, J = 7.2 Hz, 4H; -C=CH₂), 5.34 (br.d, J = 16.2 Hz, 4H; -C=CH₂), 5.90-5.98 (m, 4H; -CH=C),
25 7.52 (br, 2H; imidazole ring), 7.77 (br, 2H; imidazole

ring), 8.72 (br, 4H; Por β), 9.31 (br, 8H; β), 9.89 (br, 4H; Por β); ^{13}C NMR (150 MHz, CDCl_3) δ 30.5 (ester α), 34.6 (NCH_3), 41.8 (ester β), 65.6 ($\text{O}-\underline{\text{C}}-\text{C}=\text{C}$), 118.6 ($\text{O}-\text{C}-\underline{\text{C}}=\text{C}$), 121.6 (imidazole ring), 128.5 (Por β), 128.9 (imidazole ring), 131.4 (Por β), 132.1 ($\text{O}-\text{C}-\underline{\text{C}}=\text{C}$), 144.5-148.2 (br, 4 carbons (Por α)), 148.3 (Im $\text{N}-\text{C}=\text{N}$), 172.2 ($\text{C}=\text{O}$); UV-Vis (CHCl_3) : 709 (Abs.; 0.0537), 608 (0.0500), 474 (0.1542), 445 (0.2224), 433 (0.2186), 415 (0.2085) nm; Fluorescence (EX = 474 nm, CHCl_3) : 789, 715 nm; MALDI-TOF MASS $\text{C}_{76}\text{H}_{66}\text{N}_{12}\text{O}_8$ Calcd: 1274.51; Found: 1275.01 ($\text{M}+\text{H}$) $^+$.
Zn form of B-5 (B-6)

Saturated zinc acetate solution in methanol (1 mL) was added to porphyrin B-5 (64 mg, 50 μmol) in chloroform (3 mL). The mixture was stirred for 1 hour at room temperature, water was added to the reaction solution, then the organic layer was extracted with chloroform. The extracted organic layer was dried over anhydrous sodium sulfate and then the solvent was evaporated under reduced pressure to give B-6 (70 mg). UV (CHCl_3) : 731 (Abs.; 0.0161), 669 (0.0063), 582 (0.0036), 501 (0.0296), 462 (0.0188), 429 (0.0171) nm; Fluorescence (EX = 501 nm, CHCl_3) : 817, 740 nm; MALDI-TOF MASS $\text{C}_{76}\text{H}_{62}\text{N}_{12}\text{O}_8\text{Zn}_2$ Calcd: 1398.34; Found: 1399.21 ($\text{M}+\text{H}$) $^+$.
B-7

Zinc porphyrin B-6 (70 mg, 50 μmol) in chloroform

(2 mL) was stirred under N₂ atmosphere. Thereafter, the ruthenium carbene complex (1 mg, 10 μ mol) was added to the solution. The reaction solution was stirred for 3 hours at room temperature, water was added to the reaction solution, and then the organic layer was extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and then the solvent was evaporated under reduced pressure. The thus obtained crude product was loaded on gel column chromatography (eluent: chloroform/methanol (9 : 1)) to give B-7 (54 mg) fixed with covalent bonds. The obtained B-7 was analyzed by using a size exclusion column chromatography (JAIGEL-2.5HA), and the chromatogram shown in FIG. 2 was obtained. As a result of comparison with the polystyrene reference substance, it was confirmed that a polymer which exhibits the distribution maximum of the molecular weight thereof in the vicinity of 20,000 had been generated. The result of the MALDI-TOF MASS spectrometry of B-7 is shown in FIG. 3. In the compound B-7, the carbon-carbon bond cleavage reaction occurs at the bis-acetylenic site thereof during the measurement of mass spectroscopy, and thus peaks are observed at the molecular weights which correspond to multiples of the porphyrin unit. The largest value of the molecular weights indicated by these peaks reaches or exceed 6000. The peak in the vicinity of the molecular weight of 6742 corresponds to

the porphyrin decamer. On the contrary, no peaks which correspond to the fragments whose molecular weight is 2000 or more were observed in the compound B-6 which had not been subjected to the fixation. From these results, it is apparent that stability of the polymer has been significantly enhanced by the fixation. Further, from the measurement result of ultraviolet-visible absorption spectrum of the compound B-7 in pyridine, it was confirmed that the assembled structure of the compound was maintained.

FIG. 4 shows the ultraviolet-visible absorption spectrum (UV-Vis spectrum), in chloroform, of the polymer B-7 which has been subjected to fixation.

FIG. 5 shows the ultraviolet-visible absorption spectrum, in pyridine, of the polymer B-7 which has been subjected to fixation. FIG. 6 shows the ultraviolet-visible absorption spectrum (UV-Vis spectrum), in pyridine, of the polymer B-6 which has not been subjected to the fixation. The data of zinc

porphyrin B-6 which has not been subjected to the fixation shows that B-6 is completely dissociated to monomers in pyridine, and the large absorption peak at 453 nm in FIG. 6 is a peak which is characteristic to such a monomer. On the contrary, in the spectrum data of the polymer B-7 which has been subjected to the fixation, the peak thereof corresponding to the large absorption peak of B-6, observed in pyridine solvent,

is not large (refer to FIG. 5) but rather similar to the corresponding peak in the spectrum observed in chloroform solvent (refer to FIG. 4). This result indicates that the polymer fixed with covalent bonds of the present invention exists with remaining the polymer structure thereof even in a polar solvent. Therefore, it is now possible, according to the present invention, to provide a sample of a porphyrin array that allows evaluation of function in a polar environment.

GPC (CHCl₃, flow rate: 1.25 mL/h, detected 459.82 nm) 9.936 min; UV (CHCl₃) : 731 (Abs.; 0.0163), 581 (0.0081), 500 (0.0364), 460 (0.0328), 427 (0.0368); (pyridine) : 727 (0.0078), 665 (0.0066), 579 (0.0055), 492 (0.0212), 456 (0.0280), 433 (0.0272) nm; Fluorescence (EX = 501 nm, CHCl₃) : 817, 740 nm; MALDI-TOF MASS Calcd.: 1346 (monomer), 2692 (dimer), 4038 (trimer), 5384 (tetramer), 6730 (pentamer); Found: 1346, 2692, 4039, 5388, 6742.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.